Healing LER using directed self assembly: treatment of EUVL resists with aqueous solutions of block copolymers

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ABSTRACT

Overcoming the resolution-LER-sensitivity trade-off is a key challenge for the development of novel resists and processes that are able to achieve the ITRS targets for future lithography nodes. Here, we describe a process that treats lithographic patterns with aqueous solutions of block copolymers to facilitate a reduction in LER. A detailed understanding of parameters affecting adhesion and smoothing is gained by first investigating the behavior of the polymers on planar smooth and rough surfaces. Once healing was established in these model systems the methodology is tested on lithographically printed features where significant healing is observed, making this a promising technology for LER remediation.

Keywords: Directed self assembly, line edge roughness, block copolymer, polymersomes, electrostatic

1. INTRODUCTION

The invention of chemically amplified resists over thirty years ago was a defining point in the semiconductor industry. The high sensitivity of the resists was a key factor in facilitating manufacture of integrated circuits in high volumes. The underlying chemistry of this process involves the generation of photoacids via photodecompositions of so called photoacid generators, where the photoacids catalyse the deprotection of tertiary esters in the resist polymer. Since the reaction is catalytic one photoacid can deprotect many tertiary esters. This chemical change transforms a hydrophobic polymer into a hydrophilic polymer, allowing selective dissolution of the irradiated areas with an aqueous base. The photoacids that are formed are capable of diffusing through the film and when feature sizes were large, this did not constitute a problem, however, as the size of features has continued to decrease, diffusion of the photoacid started to affect pattern fidelity, which is commonly described as line edge roughness (LER). With the introduction of extreme ultraviolet lithography with a photon energy in the order of 92 eV, shot noise has also been recognized as a major cause of LER. It is well known that LER is linked to the printing resolution and the sensitivity of the resist, and is often described as the resolution-line edge roughness-sensitivity (RLS) trade-off, where it is a key aim for photoresists to simultaneously improve RLS.

There has been much work on the development of novel resists to overcome the RLS trade-off. Apart from resist optimisation, more radical solutions include polymer bound PAG resists,[1-7] molecular glass resists[8-16] and chain scissioning resists.[17-26] Polymer bound PAG resists, in particular, have been successful in EUVL, although improvements are still required for achieving the ITRS goals. Alternative lithography techniques such as directed self assembly (DSA) of block copolymers have also been raising significant interest, because of their ability to form small ordered features.[27-37] For example, applications in pattern multiplication and shrinking (such as contact hole shrinking), and high density storage have been demonstrated. DSA is a technique that brings together lithography (top-down) to fabricate patterns that guide the self assembly of diblock copolymers (bottom-up). The end result is ordered features with sub-lithographic resolution. A diblock copolymer is comprised of two chemically-distinct polymer chains that are covalently linked. When the blocks are immiscible they are capable of forming an array of highly-ordered nanostructures. The ultimate morphology is dependent on the relative volume fraction each block, the total molecular weight (N) and degree of immiscibility (χ). Oriented patterns with a lamellar morphology that have been fabricated by

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DSA have been shown to have a smaller LER[38] than the lithographic features that were used to guide them. This observation can be attributed to the favourable thermodynamic forces for forming smooth interfaces with minimised free energy. There are two commonly used techniques associated with DSA, namely chemo-epitaxy and grapho-epitaxy. Chemo-epitaxy of block copolymers is reliant on the chemical patterning of surfaces, where typically one of the components of the pattern preferentially interacts with one of the blocks and drives the ordered self assembly. Grapho-epitaxy uses lithography-defined surface topography to guide self assembly. Polystyrene-*block*-poly(methyl methacrylate), or PS-*b*-PMMA, is the most widely studied system, where directed self assembly of PS lines with a pitch of ~20 nm half pitch has been demonstrated.[38] However, PS-*b*-PMMA requires annealing at elevated temperatures (above 200 °C), or solvent annealing, both of which can damage a resist template or require the template to be prepared from a negative tone resist,[39, 40] or a positive tone resists that has undergone a freezing process.[38, 41, 42]

PS-*b*-PMMA has some limitations in its scalability and compatibility for future nodes of fabrication for the following reasons; (a) it has a small Flory-Huggins polymer-polymer interaction parameter (χ = 0.04 [43]) limiting the ultimate resolution, (b) annealing temperatures are significantly higher than the glass temperature (T_g) of typical positive tone photoresists. Furthermore, the reported etch selectivity of PS-*b*-PMMA is not high, which limits the ability to transfer patterns into a substrate. As a result, next generation materials that are more compatible with current lithographic processes are being actively studied. Recently, we have reported our investigations of a high χ BCP, polystyrene-*b*-poly(DL-lactide) (PS-*b*-PLA) (χ = 0.217), which overcomes some of these issues. The high χ parameter enables much smaller domain sizes, where Zalusky and co-workers have reported domains as small as 5 nm in the bulk.[44] Our initial efforts revolved around identifying the interfacial interactions of PS-*b*-PLA with substrates that were modified with crosslinked mattes of statistical copolymers of PS and PMMA.[45] It was also reported that lamella domains as small as 8 nm could be achieved. This system has also been used to conduct graphoepitaxy based DSA, where it was found no resist freezing step was required when using a model polyhydroxystyrene based photoresist template. This was because the BCP spin coating solvent was a non-solvent for the photoresist and the annealing temperature required to induce order was below the T_g of the photoresist.[46] When the width of the trench was in the order of 2 long periods (L_0) of the block copolymer, a thin wetting layer of PLA coated the sidewalls of the resist, and 3 full sized domains of PS-PLA-PS resided in the trenches. The central PLA domain could be selectively removed by RIE. This effectively shrunk the trench width from 48 nm to 12 nm, where the resulting PS sidewalls were smoother surfaces with respect to the guiding resist sidewall. The LER healing capacity of this system is limited to a relatively narrow CD range, where increasing the CD beyond 2.5 L_0 will result in multiplication, which can be advantageous but is not always desired.

Here we discuss the remediation of LER of resist patterns which is compatible with a much broader range of CDs and in theory should be compatible with typical chemically amplified resists. Rather than depositing a BCP that fills the trench we coat the sidewalls of resists with BCP which is directed through electrostatic interactions. The wafer is then selectively annealed allowing reorganisation of the polymer chains in the block copolymer but not in the resist. This is made possible because the BCP has been designed to have a T_g that is less than that of the resist, but greater than room temperature.

2. EXPERIMENTAL

Detailed synthesis and characterisation of poly(DMAEMA)-*b*-poly(tBuMA), and crosslinkable statistical copolymers of PMMA and poly(tert butyl methacrylate), as well as methods for surface modification and roughness healing are detailed in a recent publication.[47]

3. RESULTS AND DISCUSSION

3.1 Rationale for Polymer Synthesis

The rationale for the design of the block copolymer was to include a block that was capable of carrying a positive charge to direct the assembly of the BCP to lithographic sidewalls that are negatively charged, while the second block was required to have a T_g less than typical photoresists, but higher than room temperature. Having such an intermediate T_g allows the BCP to be selectively annealed such that the polymer chains can undergo reorganization to minimize the free energy at the polymer-air interface. The charged block was comprised of repeat units that contain a pendant tertiary amine group, which can carry a positive charge in acidic aqueous solutions. The second block contains tertiary butyl methacrylate repeat units. Reversible addition-fragmentation chain transfer (RAFT) polymerization, a method for

controlled free radical polymerization was used to prepare the block copolymers. This method can give polymers with controlled molecular weights and low polydispersities.[48, 49] Figure 1 shows the reaction scheme for the synthesis of poly(tBuMA), which was followed by chain extension with DMAEMA to yield the block copolymer. Figure 1 also shows the molecular weight versus conversion plots for these two steps, where a linear relationship can be observed. This data allows a particular molecular weight to be selected by conducting the polymerization for a given time. The resulting polymers can be seen to have low polydispersities (Figure 1).

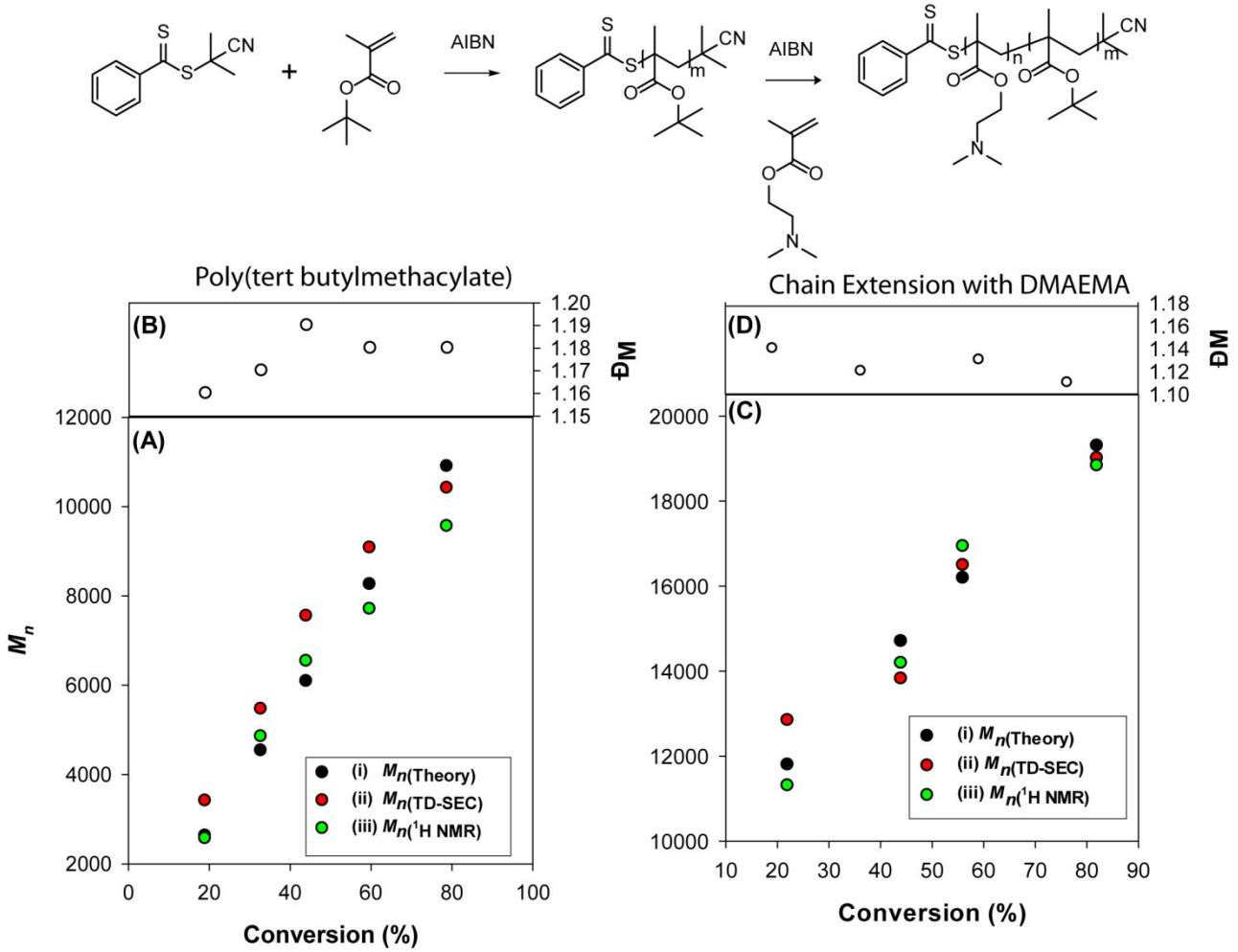

Figure 1 (Top) Reaction scheme for synthesis of poly(tBuMA) and chain extension with DMAEMA (bottom left) M_n versions conversion plot for polymerisation of tBuMA and (bottom right) M_n versions conversion plot for chain extension with DMAEMA.

3.2 Solution properties of the block copolymer and adhesion to planar negatively charged surfaces

poly(DMAEMA)-*b*-poly(tBuMA) is an amphiphilic polymer, so can undergo self assembly in aqueous solutions to form micellar structures. To achieve this the polymer was first dissolved in tetrahydrofuran, a good solvent for both blocks, and then water was added drop-wise. Following this the solvent was removed by evaporation under reduced pressure and the pH was adjusted to 6.4. Cryo-TEM of the aqueous solutions revealed that polymersomes had formed with a diameter of 18 ± 2 nm.[47] This is represented schematically in Figure 2 A.

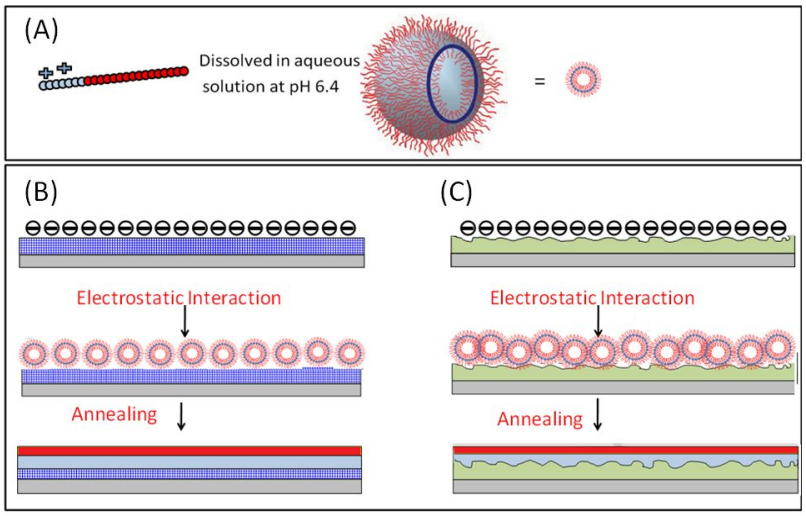

Figure 2 (A) The block copolymer at 0.6 mg/mL solution and pH 6.4 forms vesicles. These vesicles were dip coated on (B) a flat surface or (C) a rough surface. The annealing effects on both surfaces were studied by using AFM.

To help understand the fundamentals of adhesion of the positively charged polymersomes to surfaces a model substrate was required as a test vehicle. To this end, silicon wafers were modified with a crosslinked matte which contained carboxylic acids to give a flat surface with a negative charge, similar to that of lithographic sidewalls. These substrates were dip coated in solutions of poly(DMAEMA)-*b*-poly(tBuMA), with BCP concentrations of 1×10^{-5} mg/mL up to 1.2 mg/mL. The substrates were then rinsed with ultrapure water and dried with a stream of nitrogen gas. This process is shown schematically in Figure 2 B. The samples were analyzed by atomic force microscopy (AFM) to determine the surface morphology following treatment. The AFMs are shown in Figure 3, where it can seen that the coverage of the polymersomes increases to a maximum at about 0.6 mg/mL, so this concentration was selected for further studies.

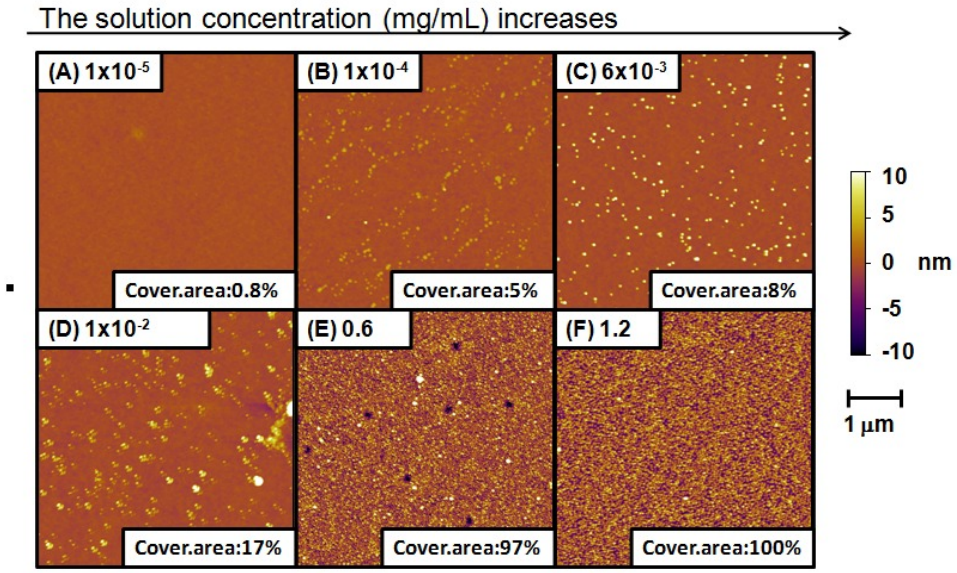

Figure 3 The negatively-charged surface was dipped coated in different PDMAEMA-*b*-P*t*BuMA concentrations, (A)10^{-5}, (B) 10^{-4}, (C) 6×10^{-3},(D) 10^{-2}, (E) 0.6 and (F) 1.2 mg/mL. The coverage of the polymersomes increased from (A) 0.8%, (B) 5%, (C) 8%, (D) 74%, (E) 97%, (F) 100%.

To obtain spectroscopic confirmation of adhesion the substrate modified with the 0.6 mg /mL solution of the polymersomes was also characterised using X-ray photoelectron spectroscopy (XPS), a surface sensitive analysis

technique. Figure 4 shows a series of XPS survey spectra of the wafer modified with a crosslinked matte, the wafer modified with a crosslinked matte and rinsed with ultrapure water, the modified wafer treated with polymersomes and finally the modified wafer treated with polymersomes and then rinsed with ultrapure water. The wafers that had not been treated with polymersomes did not exhibit a peak in the N (1s) region (~400 eV), but after dip-coating, a peak was observed at approximately 402 eV. The negatively charge surface is composed of only carbon, oxygen and hydrogen atoms so no nitrogen signal would be expected for those samples. On the other hand, the BCP that makes up the polymersomes contains poly(DMAEMA) which is a nitrogen containing polymer, so the observation of the N (1s) signal after dip coating and washing is consistent with adhesion of the polymersomes to the substrate and supports the AFM results.

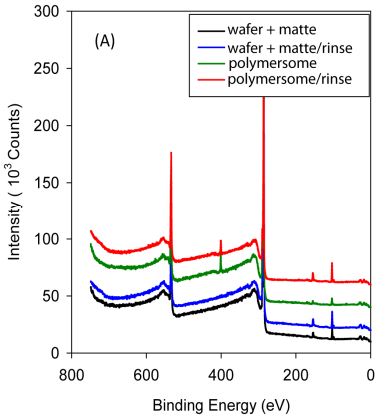

Figure 4 XPS survey spectra of wafer modified with a crosslinked matte (black), wafer modified with a crosslinked matte and rinsed with ultrapure water (blue), modified wafer treated with polymersomes (green) and modified wafer treated with polymersomes and treated with ultrapure water (red).

3.3 Understanding the effect of Annealing on BCP Morphology

In this study annealing is carried out following deposition to cause reorganisation of the polymer chains, where smoothing of the surface morphology will be driven by minimisation of the free energy at the polymer air interface. Differential scanning calorimetry (DSC) was used to measure the T_g of the a BCP, which was found to be 67 °C, it was expected that the polymer could undergo reorganisation when annealed above this temperature. The substrate modified with the 0.6 mg solution of polymersomes was subjected to annealing at 120 °C, which is higher than the T_g of the BCP, but lower than the T_g of typical photoresists. Figure 5 shows AFM micrographs of the substrate, a) before treatment b) after dip coating and rinse and c) after annealing. The initially smooth surface (RMS 0.3 ± 0.5 nm) becomes rough (RMS 1.6 ± 0.5 nm) after being coated with the polymersomes and then following annealing to 120 °C this roughness decreases to 0.4 ± 0.2 nm, which was not significantly different to the original substrate. These results suggest that annealing of the polymersomes to 120 °C provides sufficient kinetic energy for the polymer chains in the block copolymer to reorganise and destroy the kinetically trapped polymersome structure that is deposited on the substrate

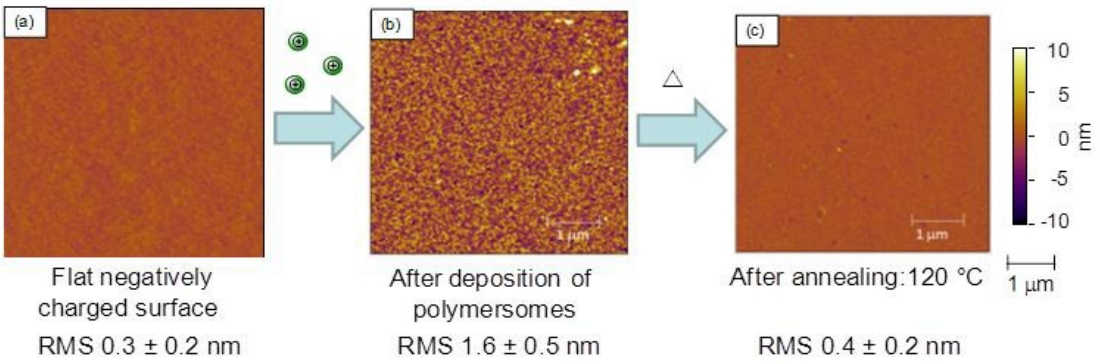

Figure 5 AFM micrographs of: a) A flat negatively charged surface (Si wafer modified with a crosslinked matte), b) after dipcoating with a 0.6 mg/mL solution of polymersomes and c) after annealing to 120 °C for 10 minutes.

Having established that the polymersomes can adhere to negatively charged surfaces and then undergo reorganisation during an annealing process ,the next step was to determine if this methodology could be used to heal surface roughness. The test vehicle that was selected to do this in the first instance was a planar rough surface which was prepared using methodology established by Prabhu and coworkers.[50] Briefly, this involved generating a two layer film on a silicon wafer, where the bottom layer was comprised of a poly(hydroxystyrene) based resist polymer that does not contain a photoacid generator. The top layer, or photoacid feeder layer, was comprised of a resist polymer that contained PAG. During irradiation the PAG in the top layer undergoes photoinduced reactions to yield photoacids. The photoacids catalyse the deprotection of hydrophobic tertiary esters in the resist polymer in the top layer which switches its solubility during an annealing step (PEB). This photoacid is also capable of diffusing into the bottom layer as a front where it can catalyse reactions that switch the solubility of the resist polymer in the areas it diffuses to. When the film is treated with aqueous base the top layer and a portion of the bottom layer is removed. Since the diffusion is stochastic the surface morphology of the remaining photoresist will be rough on a similar length scale as to what is achieved in for features printed by photolithography.

An AFM micrograph of the planar rough surface is shown in Figure 6 a) and it was determined to have an RMS roughness of 2.4 ± 0.5 nm. This substrate was dip coated in 0.6 mg/mL solution of the polymersomes, rinsed with ultrapure water and then dried with a stream of nitrogen. An AFM micrograph of this is shown in Figure 6 b) where the roughness does not significantly change (2.2 ± 0.5 nm) compared to Figure 6 a), although a change in morphology can be observed which is consistent with the adhesion of the polymersomes. The sample was then annealed at 115 °C for 10 minutes, which was lower that the T_g of the underlying PHOST resist polymer. The RMS roughness was found to drop to 0.7 ± 0.4 nm after annealing of the polymersome treated surface, but an untreated control did not change in morphology when annealed to this temperature (micrograph not shown). These experiments demonstrate our initial hypothesis that block copolymers can be used to heal nanoscale surface roughness.

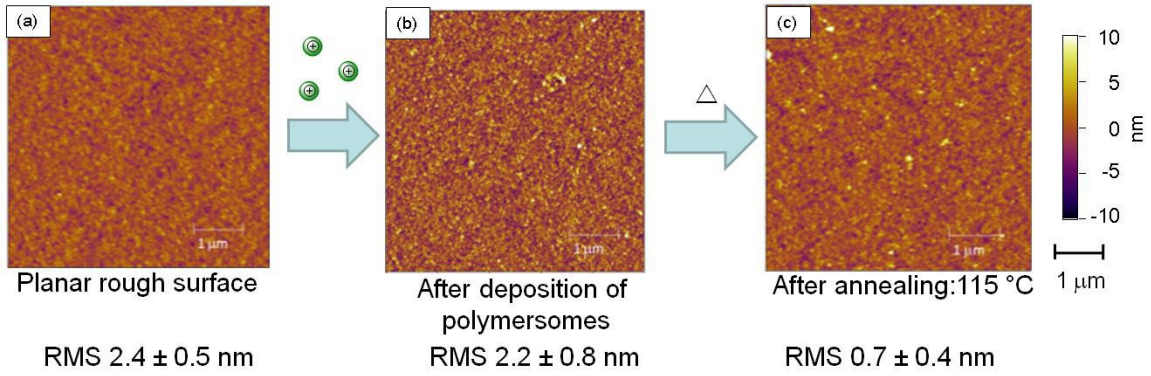

Figure 6 AFM micrographs of a) a planar rough surface, b) after deposition of polymersomes an c) after deposition of polymersomes and annealing at 115 °C.

3.4 Healing of Lithographic Patterns

After demonstrating that the polymersomes could be used to heal planar rough surfaces, the next test vehicles selected were line-space patterns prepared by electron beam lithography (EBL). The same PHOST based resist was used to prepare the line-space patterns with a trench width of 174 ± 5 nm and a 3σ LER of 5.8 ± 0.4 nm and top a representative top down SEM is shown in Figure 7 a). The patterned substrate was then dip coated with a 0.6 mg / mL solution of the polymersomes and an SEM is shown in Figure 7 b). The width of the trench reduced to 166 ± 21 nm, but the 3σ LER did not significantly change (5.7 ± 0.4 nm). This is consistent with the behaviour observed in the study using planar rough surface described above. The sample was then annealed at 100 °C (SEMs in Figure 7 c), and it was found that the trench width decreased to 160 ± 1 nm and the roughness decreased to 3.4 ± 0.3 nm. A control that was not treated with polymersomes, but did undergo the annealing step was found not to have any significant change in trench width or LER. To better understand the frequencies of roughness that were being healed a PSD analysis was conducted and this has been plotted in Figure 8. The PSD plot is consistent with the progression of the roughness during the treatment process described above. For example, decreases in roughness were observed over all frequencies for the sample that was treated with polymersomes and then annealed. Furthermore, the controls (polymersome treated/ not annealed and not treated with polymersomes/ annealed) did not show an significant change in roughness.

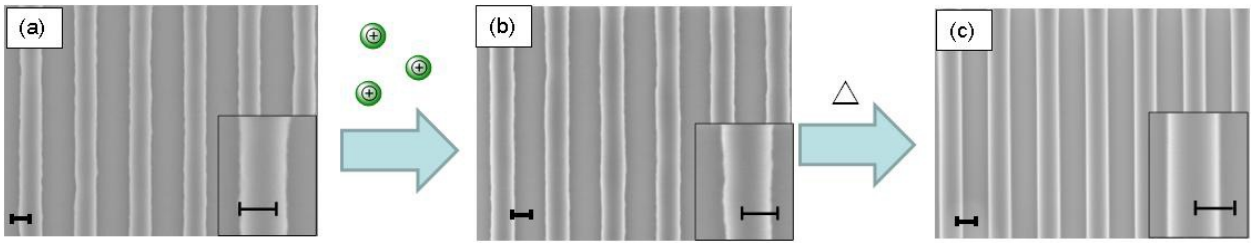

Figure 7 Top-down SEMs of a) EBL patterned PHOST resist (no treatment) b) after treatment with polymersomes and c) after treatment with polymersomes and annealing.

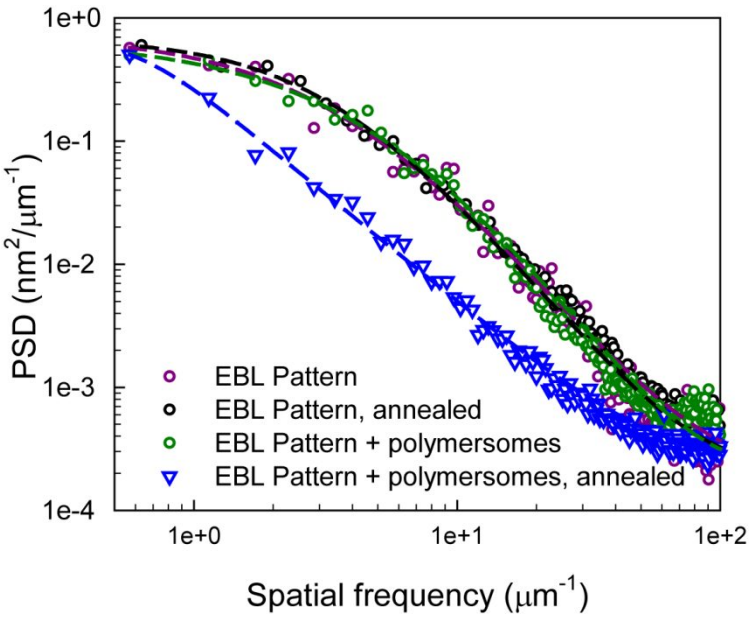

Figure 8 PSD versus spatial frequency plots for images in Figure 7.

4. CONCLUSIONS

This paper described the use of aqueous solutions of block copolymers to remediate LER of an EUVL based resist. The block copolymers were rationally designed to serve this function. One block was capable of carrying a positive charge, which facilitated the adhesion of the polymers to resist sidewalls, while the second block was designed to have a T_g value that was less than that of the typical resist polymers but greater than room temperature. This intermediate T_g facilitates selective annealing of the BCP such that the polymer chains can undergo reorganization to minimize the free energy at the polymer-air interface. Adhesion was demonstrated through AFM and XPS experiments on planar negatively charged surfaces. AFM of these treated planar surfaces following annealing above the T_g of the BCP showed that the surface morphology could undergo reorganization. Studies using planar rough surfaces showed that healing of the nanoscale roughness by as much as 71% could be achieved following treatment and annealing. Finally, the concept was demonstrated on lithographic features where healing of 41 % was achieved.

5. ACKNOWLEDGEMENTS

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